



An examination of potential controls on shell Mn/Ca ratios in the calcite of the bivalve *Mytilus edulis*

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The Mn/Ca ratios in the calcite of marine bivalves have been suggested to reflect both the dissolved and/or particulate Mn concentrations of seawater. However, a clear understanding of what controls shell Mn/Ca ratios is still lacking and a clear quantitative relationship between dissolved and/or particulate Mn and shell Mn/Ca ratios in either calcitic or aragonitic molluscs must be established and validated before any application of a bivalve Mn/Ca palaeoproxy. To study the influence of seawater dissolved and particulate Mn concentrations on bivalve shell calcite Mn/Ca ratios, *Mytilus edulis* specimens were grown in a field experiment in the Menai Strait, U.K., for a one-year period. A single maximum ($0.54 \mu\text{M}$) during spring dominated the annual variation of seawater dissolved Mn concentrations, while seawater particulate Mn concentration was highest (up to $0.18 \mu\text{M}$) during autumn and winter, although smaller increases in particulate Mn during the phytoplankton spring bloom were also observed. In *M. edulis*, shell Mn/Ca ratios of newly precipitated calcite showed a double-peak annual variation with maximum values (up to 0.19 mmol/mol) during early spring and early summer. None of the two maximum of shell Mn/Ca ratios can be explained by an increase in either seawater dissolved or particulate Mn concentrations. Shell Mn/Ca ratios thus were not controlled by dissolved or particulate Mn concentrations. In *M. edulis*, the double-peak seasonal variation of shell Mn/Ca ratios was remarkably similar to the seasonal variation of shell growth rates. However, the influence of shell growth rate on shell Mn/Ca ratios is the opposite of the inverse relationship observed unequivocally between precipitation rate and Mn partition coefficient in synthetic inorganic calcite, and thus must reflect a physiological influence on shell Mn content.